

# Rate constants for formation of NO in vibrational levels $v=2$ through 7 from the reaction $N(^4S) + O_2 \rightarrow NO^v + O$

A. Rahbee and J. J. Gibson

Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts 01731  
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Vibration-rotation spectra of the  $\Delta v = 2$  sequence of the nitric oxide formed by the chemiluminescent reaction  $N(^4S) + O_2 \rightarrow NO(X^2\Pi) + O$  have been obtained with a spectral resolution of  $15\text{ cm}^{-1}$ . Emission bands due to  $N_2O$  were observed to occur in the same spectral region as the first overtone of NO. These were experimentally eliminated and the resulting NO spectra were used to derive rate constants for formation of NO in vibrational levels  $v = 2$  through  $v = 7$ . In units of  $10^{-19}\text{ cm}^3/\text{sec}$ , these room temperature rate constants are, respectively,  $55 \pm 14$ ,  $57 \pm 9$ ,  $33 \pm 3$ ,  $24 \pm 4$ ,  $7 \pm 2$ , and  $5 \pm 2$ . Of all the nitric oxide molecules formed in the reaction, only 18% are formed in levels  $v \geq 2$ . In terms of energy, of the 1.39 eV exothermicity of the reaction, about 10% goes into vibrational energy in levels  $v \geq 2$ .

## I. INTRODUCTION

The reaction of ground state nitrogen atoms with oxygen molecules leading to formation of nitric oxide is of considerable interest in interpretation of auroral phenomena and more generally in determination of the degree of excitation of the product NO molecules. Infrared emission measurements are often useful in studying vibrationally excited products in chemiluminescent reactions. The technique was employed in this laboratory to study  $N(^4S) + O_2 \rightarrow NO^v + O$  ( $v$  indicates vibrational excitation) under low spectral resolution.<sup>1</sup> In that experiment, it was shown that the reaction was chemiluminescent and from the envelope of the spectrally unresolved first overtone vibration-rotation bands of NO, some information regarding the excited state yield of the reaction was deduced. Subsequently, a photon efficiency figure for the reaction was reported.<sup>2</sup> In the analysis of the results of that investigation, the only loss mechanism for the NO molecules was assumed to be the very fast reaction  $N + NO \rightarrow N_2 + O$ . Estimates for the quenching rate of  $NO^v$  by  $O_2$  indicated this loss mechanism to be unimportant. It was also shown that in the pressure region employed, no redistribution among the vibrational levels occurred; whereas the NO rotational distribution quickly attained equilibrium with the gas mixture. The NO overtone band shapes could be described by independent vibrational and rotational temperature. Due to lack of resolution, unknown spectral features could not be distinguished and a molecular band at  $\sim 2.25\text{ }\mu\text{m}$  could not be identified for the same reason. Since these early results, quenching of  $NO^v$  by  $O_2$  has been studied and measured by Murphy *et al.*, and is shown to be significant.<sup>3</sup> Whitson *et al.*,<sup>4</sup> have also measured the quenching of  $NO^v$  by  $O_2$  and report rates for  $v = 2$  through 7. In addition, they have reported an initial vibrational distribution for  $NO^v$  from  $N + O_2$  reaction using a slightly resolved experimental spectra of the NO overtone band.

More recently, the reaction of  $N(^2D)$  with  $O_2$  was studied by Kennealy *et al.*<sup>5</sup> in a cold environment to suppress the  $N(^4S) + O_2$  reaction whose rate constant exhibits a very large temperature dependence. Consequently, no information on the latter reaction was obtained, but values for the partial rate constants for the  $N(^2D)$  reaction were reported.

To refine and augment the previous results obtained on  $N + O_2$  reactions, the present interferometric study was undertaken to obtain resolved spectra of the NO first overtone, to identify the unknown molecular band referred to above, to ascertain that the NO emission bands were free from other molecular emissions, and finally to derive a set of detailed rate constants for formation of NO in level  $v$ , taking into account the quenching of vibrationally excited NO by  $O_2$ .

Section II describes the experimental procedures and results. Section III is a discussion of these results and conclusions drawn from the experiment.

## II. EXPERIMENTAL

A schematic of the experimental apparatus is shown in Fig. 1, which is essentially identical to that used in Ref. 1 with the exception that the circular variable filter was replaced by a Michelson interferometer-spectrometer for the purpose of obtaining the vibrational structure of the NO first overtone bands. Nitrogen atoms produced in the microwave cavity flow into the reaction vessel which is a 2 l gold-coated integrating sphere with ports for pumping, gas admission, and pressure measurements. To increase the efficiency, the sphere was cleaned and freshly gold coated for this experiment. The nitrogen atom density as measured by the NO titration method was generally found to be approximately  $7 \times 10^{13}\text{ cm}^{-3}$ . Background molecular nitrogen pressure in the sphere was usually 250 mTorr. The oxygen pressure was varied over the range of 200 to 600 mTorr. Below this pressure, the signal to noise ratio was too low for meaningful measurements.

The interferometer was equipped with 1 in. optics and had a 1 cm maximum optical path difference as the continuously driven moveable mirror travelled between extreme positions. The central fringe was imaged by a  $f/1.0$  silicon lens onto a  $2 \times 2\text{ mm}$  lead sulfide detector cooled to 193 K. The interferogram was digitized at successive intervals determined from the zero crossings of a 6328 Å He-Ne reference laser. Spectra were recovered by taking the Fourier transform of digitized interferograms. The instrument function was measured by observing the  $4852.2\text{ cm}^{-1}$  helium line. Spectral re-

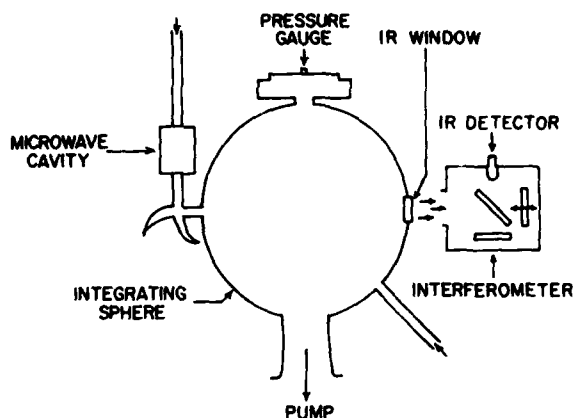
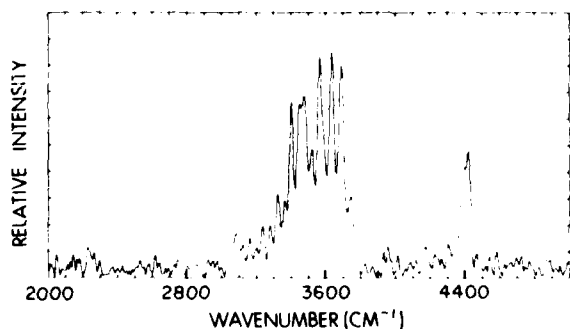
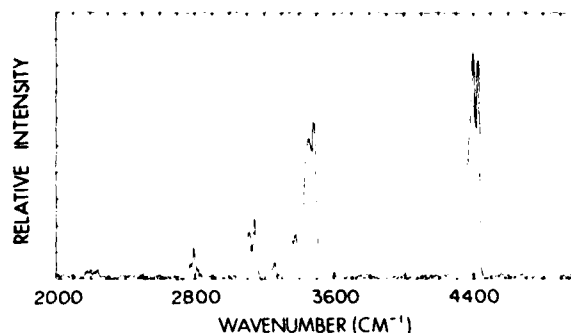


FIG. 1. Schematic diagram of the apparatus.

sponse was determined by calibration with a standard 1000 °C blackbody.

Several preliminary experimental runs to obtain resolved spectra of the first overtone of NO were made with the  $O_2$  pressure fixed at 500 mTorr. A typical spectrum is shown in Fig. 2. Additional measurements over the oxygen pressure range of 200–300 mTorr produced spectra similar to the one shown. The appearance of the spectra in the 3100–3500  $cm^{-1}$  region was persistently repeatable. Existence of these emission bands would indicate populating NO vibrational levels higher than allowed by 1.39 eV exothermicity of the reaction  $N(^4S) + O_2 \rightarrow NO^+ + O$ . Thus, the conclusion is that the bands in the 3100–3500  $cm^{-1}$  region are due to species other than NO. This is supported by the observation of the band at 4450  $cm^{-1}$  which is highly pronounced and is identified as the  $00^0_2 - 00^0_0$  transition of the electronic ground state of  $N_2O$ . This is the band observed at 2.25  $\mu m$  in the low resolution experiment.<sup>1</sup> The  $\nu_3$  mode of  $N_2O$  which occurs at 2225  $cm^{-1}$  can also be discerned in Fig. 2 although the detector sensitivity in this region has fallen off considerably. The other two infrared fundamental modes at 1277 and 589  $cm^{-1}$  ( $\nu_1$  and  $\nu_2$ , respectively) are entirely out of the spectral range of the detector. Nevertheless, other  $N_2O$  combination bands can overlap the NO first overtone range. In particular, bands at 3365 and 3481  $cm^{-1}$ ,

FIG. 2. Spectrum obtained at  $O_2$  pressure of 500 mTorr. NO overtone spectral region is 3300 to 3800  $cm^{-1}$ .FIG. 3.  $N_2O$  spectrum obtained in vibrational exchange between pure  $N_2O$  and  $N_2^+$ .

both being transitions to the  $(00^0_0)$  state of  $N_2O$ , would be expected to make radiative contributions and their existence is suggested in the spectrum shown in Fig. 2.

If  $N_2O$  is either formed chemically or exists in the chamber as trace impurity, the existence of copious amounts of vibrationally excited nitrogen ( $N_2^+$ ) in the reaction cell suggests a possible source for the  $N_2O$  vibrational energy since  $N_2O$  undergoes rapid vibrational exchange with  $N_2^+$  as shown in other investigations.<sup>6,7</sup>

Figure 3 shows an  $N_2O$  infrared spectrum obtained in vibrational exchange with  $N_2^+$ . The spectrum was obtained by adding  $\approx 2$  mTorr of  $N_2O$  to discharged nitrogen. All the spectral features are attributable to  $N_2O$ . Comparison of Fig. 2 and 3 provides strong evidence that vibrational exchange between  $N_2^+$  and  $N_2O$  also occurs in the  $N(^4S) + O_2 \rightarrow NO + O$  experiment of Fig. 2.

The bands at 2225 and 4445  $cm^{-1}$ , which were referred to above, are the  $\nu_3$  and  $2\nu_3$  modes of  $N_2O$ , respectively. The former is in close energy resonance ( $\Delta E = 107$   $cm^{-1}$ ) with  $N_2$  ( $r=1$ ) and the latter ( $\Delta E = 210$   $cm^{-1}$ ) is attributed to either direct exchange with  $N_2$  ( $r=2$ ) or further exchange between  $N_2O$  ( $00^0_1$ ) and  $N_2$  ( $r=1$ ) resulting in  $N_2O$  ( $00^0_2$ ). Tentative identification of some of the other observed bands include the combination bands ( $\nu_1 + \nu_3$ ) at 3480  $cm^{-1}$  and ( $2\nu_2 + \nu_3$ ) at 3365  $cm^{-1}$ . The two bands at about 3260 and 3150  $cm^{-1}$  could be  $2(\nu_3 - \nu_2)$  and  $(2\nu_3 - \nu_1)$ , respectively, and the band at 2800  $cm^{-1}$  is  $(\nu_2 + \nu_3)$ .

Precautions were taken to assure that none of the gas supplies contained  $N_2O$ . Trapping at 77 K of the high purity research grade gases over prolonged periods produced no reduction in  $N_2O$  emissions. Spectra of discharged nitrogen were also obtained and no  $N_2O$  bands were observed, indicating it was not present or formed in the discharge flow system. All evidence points to chemical formation of  $N_2O$  when  $O_2$  and active nitrogen are mixed.

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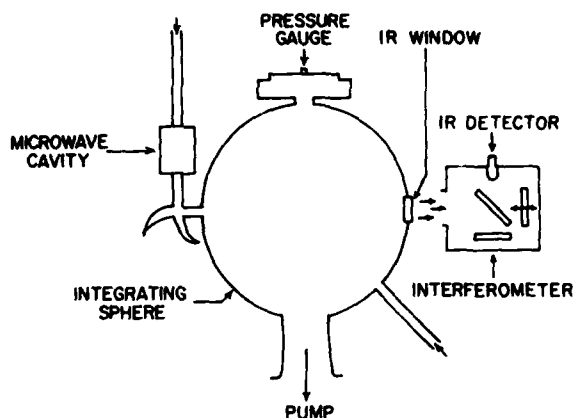
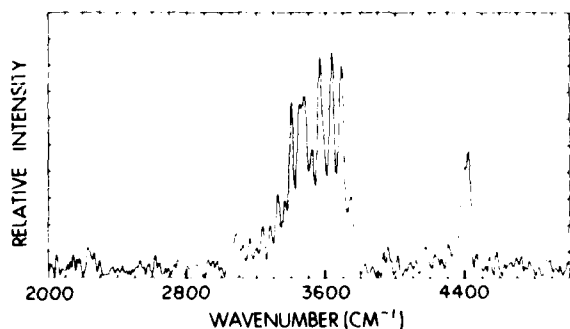
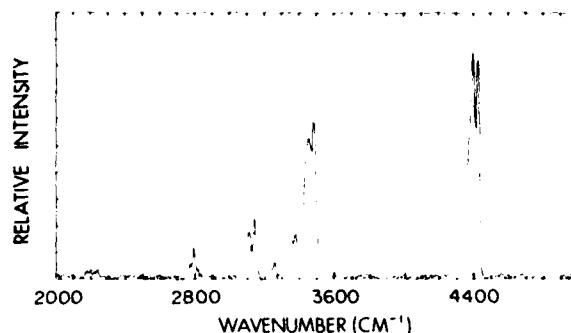


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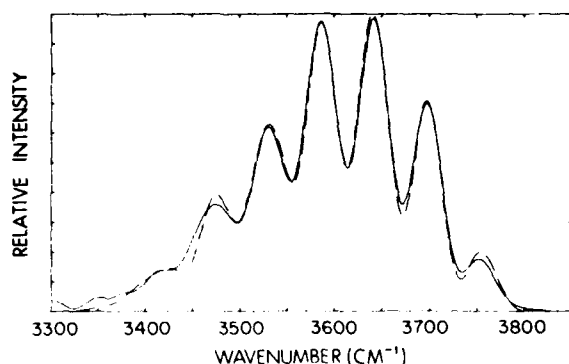


FIG. 4. NO first overtone spectrum obtained at  $O_2$  pressure of 500 mTorr. The dashed curve is calculated for best fit to the experimental result (solid curve).

Figure 4 shows the overtone band of NO obtained after elimination of  $N_2O$  emission bands in the manner just described. Although only the limited spectral range of NO overtone is shown in this figure, the  $N_2O$  bands outside this spectral range were also absent. The spectrum which is corrected for the spectral response of the optical system is a sample of results obtained over the  $O_2$  pressure range of 200 to 600 mTorr and forms the basis of the analysis of results in the next section.

$N_2O$  emission occurring in the overtone region of NO was undetectable in the low resolution experiment due to the smoothing effect of the scanning function of the circular variable filter employed in the experiment.<sup>1</sup> As a result, the value of NO overtone photons per  $O_2$  molecules reported to be  $1.5 \times 10^{-6}$  in Ref. 1 has to be corrected for contribution due to  $N_2O$  emission. The method used was to obtain the spectra with and without Pyrex wool in the discharge side of the reaction cell. Comparison of the two areas under the two spectra then furnished the relative magnitude of the  $N_2O$  and NO emissions. We found that nearly 1/3 of the signal observed was due to  $N_2O$ . This ratio was nearly the same over the  $O_2$  pressure range used. Thus, the rate of photon production per  $O_2$  molecule is revised down to  $10^{-6}$  from its reported value.<sup>1</sup> This quantity will be used in the next section to derive  $NO(r)$  number densities.

An estimate of the density for  $N_2O$  can also be obtained from the relative magnitude of the  $4450\text{ cm}^{-1}$  band of  $N_2O$  in Figs. 2 and 3. This indicated a density of  $5 \times 10^9\text{ cm}^{-3}$  for  $N_2O$  at an  $O_2$  pressure of 500 mTorr. This is only meant as an estimate since the finite pressure of oxygen molecules at the experimental conditions under which Fig. 2 was obtained may modify the nitrogen vibrational distribution. A possible mechanism for  $N_2O$  formation will be considered later in this paper. The fact that no  $N_2O$  emission was seen after elimination of  $N_2^+$  from the discharge indicates that the vibrationally excited  $N_2$  from  $N + NO \rightarrow N_2^+ + O$  is not produced at sufficient quantities to contaminate the NO spectra.

### III. RESULTS AND DISCUSSION

To obtain the observed distribution from the experimental spectra (solid curve in Fig. 4) the procedure

was to simulate the NO observed spectrum, in a manner similar to the method used by Kennealy *et al.*<sup>5</sup> At each  $O_2$  pressure, the observed spectrum was simulated through a computer program that involved calculation of line positions and intensities for each vibration-rotation band from  $r=2$  through  $r=7$ , and convolution of each band with the experimentally determined scanning function of the interferometer. The relative intensities of the NO vibration-rotation bands were fit to give the best match to the observed spectrum by multiple linear regression analysis. This simulated spectrum is shown as the dashed curve in Fig. 4 and is the calculated spectrum for the observed one shown in that figure.

The total photon emission rate of  $10^{-6}$  per s per  $O_2$  molecule<sup>1</sup> and a set of Einstein transition probabilities calculated by Billingsley<sup>9</sup> were used to convert the relative observed distribution into NO number densities. The results for the entire set of experimental spectra are shown in Table I. Extensive calculation of the error in these number densities has shown that the experimental error of 30% in photon measurements is the dominant factor and is propagated through to the number densities in Table I.

The reaction  $N(^4S) + O_2 \rightarrow NO(r) + O$ , based upon exothermicity arguments, can only populate up to and including level  $r=6$  of the product NO. Formation of NO in the  $r=7$  level is due to available kinetic energy in the relative energy distribution of the reactants beyond the activation energy. Our calculations show that this energy is sufficient to make the  $r=7$  level accessible to the product NO molecule.

Derivation of the partial rate constants from densities shown in Table I is made complicated by the fact that the nitrogen atom density in the sphere does not remain constant and varies over the residence time in the sphere of 0.5 s. Consequently, NO densities vary as functions of time. Thus, the observed densities in Table I are values time averaged over the residence time in the reaction cell and further analysis of the results requires knowledge of this variation for each level  $r$ . To do this, the important reactions influencing NO density have to be determined.

Kinetic mechanisms of importance in this experiment are

TABLE I. Observed NO densities<sup>a</sup> for  $r=2$  through 7.

$O_2$ pressure (mTorr)	NO( $r$ )					
	$r=2$	$r=3$	$r=4$	$r=5$	$r=6$	$r=7$
200 <sup>b</sup>	1.15	1.03	0.65	0.40	0.12	0.05
250 <sup>b</sup>	1.30	1.10	0.75	0.39	0.18	0.05
300 <sup>b</sup>	1.68	1.64	0.92	0.52	0.15	0.07
400 <sup>b</sup>	2.34	2.05	1.08	0.63	0.22	0.09
440 <sup>b</sup>	2.82	2.51	1.25	0.68	0.19	0.09
510 <sup>b</sup>	3.27	2.85	1.48	0.76	0.25	0.11
600 <sup>c</sup>	3.16	2.84	1.73	0.97	0.27	0.10

<sup>a</sup>Densities in powers of  $10^8$  molecules  $\text{cm}^{-3}$ .

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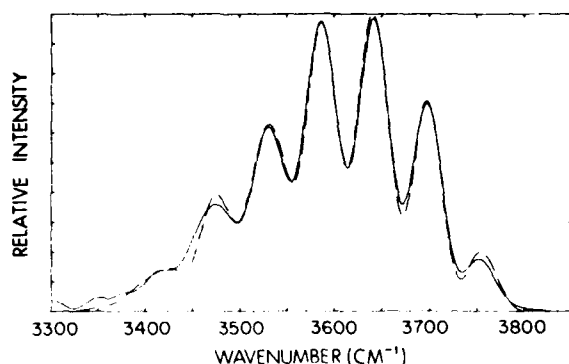


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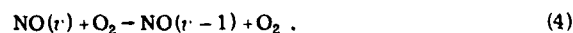
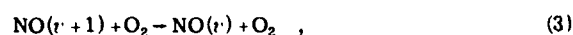


followed by the fast reaction



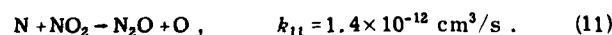
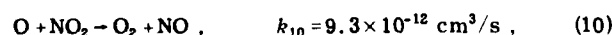
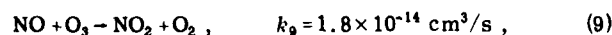
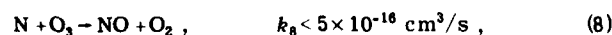
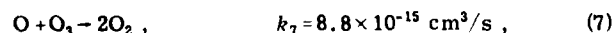
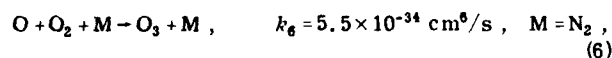
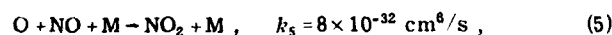
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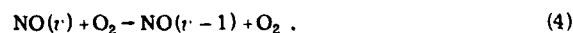
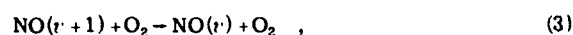


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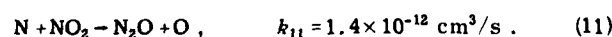
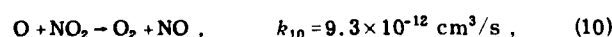
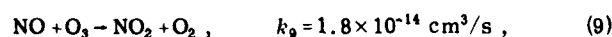
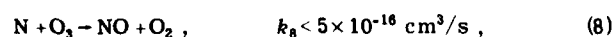
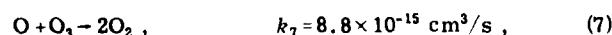
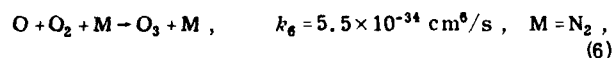
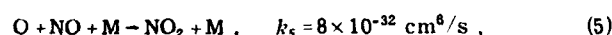
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The major conclusion of the above arguments is that the only reactions that have to be taken into consideration in the analysis of the data of Table I are Reactions (1) through (4). The effect of not taking into account the quenching Reactions (3) and (4) will be discussed below. The rate of change of NO density in vibrational level  $v$  is thus given by

$$\frac{d(NO)_v}{dt} = k_1^v(N)(O_2) - k_2(N)(NO)_v + k_q^{v+1}(O_2)(NO)_{v+1} - k_q^v(O_2)(NO)_v \quad (12)$$

There are six such rate equations, one governing the density in each level  $v$ . Nitrogen atom density ( $N$ ) itself is time dependent as mentioned above. The rate equation governing ( $N$ ) can be evaluated from Reactions (1) and (2). The computer program developed for solution of Eq. (12) first solves for this time dependence of  $N$  density and then utilizes the Runge-Kutta method of order 4 for solving simultaneous differential equations.<sup>22</sup> This method, which is essentially an iterative technique, requires (a) a starting set of values for  $k_1^v$ 's, and (b) initial values for NO concentrations. For the starting values of the rate constants we chose the solutions of Eq. (12) assuming steady state and neglecting the  $O_2$  quenching terms. The initial  $(NO)_v$  concentrations are, of course, all equal to zero. The computer program then using these values calculates the time history of NO for each level  $v$  and each oxygen pressure employed. It then calculates the time average for each  $(NO)_v$  over residence time of 0.5 s for comparison with the experimentally obtained values listed in Table I.

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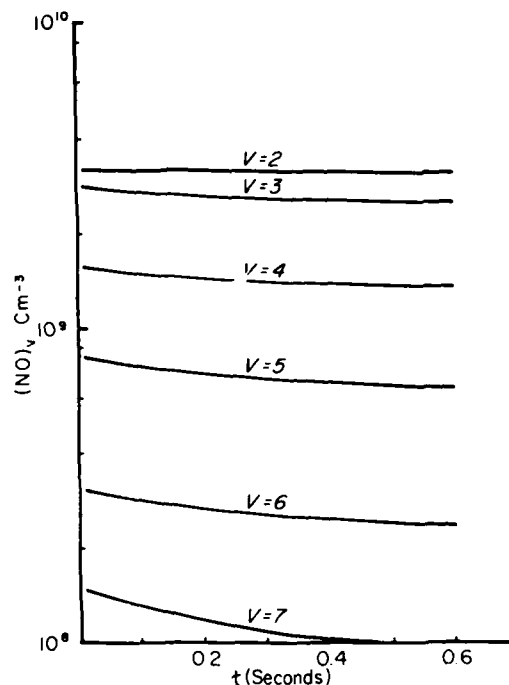


FIG. 5. Time variation of NO concentrations for the observed levels  $v=2$  through 7 and using the measured values of  $k_1^v$  shown in Table II.

II. The initial rise of this curve from zero, which is primarily determined by the time constant  $(k_2N)^{-1}$  ( $\approx 10^{-3}$  s), is not shown in Fig. 5 for clarity. The uncertainties in the rate constants shown in Table II are the results of propagation of error calculations and include uncertainties in band intensity determination and photon emission rates. The large errors in the rate for levels 2 and 3 are probably due to absorption by water vapor in the optical path of the interferometer. Levels 6 and 7 often had poor S/N ratios especially at low  $O_2$  pressure and consequently show large uncertainties in their rates. The sum of the rates in Table II is  $0.18 \times 10^{-16}$  cm<sup>3</sup>/s, which compared to the total rate of formation of NO of  $10^{-16}$  cm<sup>3</sup>/s shows that only 18% of all NO product molecules are initially formed in levels  $v=2$  while the remainder of the 82% is shared in levels  $v=0$  and 1. The sum of the rates for these two levels is  $0.82 \times 10^{-16}$  cm<sup>3</sup>/s and at the present time there is nothing in the experiment to point to individual rates for levels  $v=0$  and 1. Considering the observed levels  $v=2$  to 7, from the point of view of energy, of the 1.39 eV exothermicity of the  $N + O_2 \rightarrow NO + O$  reaction, only about 0.14 eV or 10% shows up in vibrational energy levels  $v=2$ . The overall result then is that the reaction does not populate the higher vibrational levels of the product NO molecule effectively.

This general result has been independently confirmed by Whitson *et al.*<sup>4</sup> in their experiment which measured only relative values for initial vibrational distribution. Their results basically exhibit the same value for the first four observed levels whereas the present results, except for  $v=2$ , monotonically decrease as a function

TABLE II. Partial rate constants for formation of vibrationally excited NO in the  $N(^4S) + O_2 \rightarrow NO^{\dagger} + O$  reaction.

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The major conclusion of the above arguments is that the only reactions that have to be taken into consideration in the analysis of the data of Table I are Reactions (1) through (4). The effect of not taking into account the quenching Reactions (3) and (4) will be discussed below. The rate of change of NO density in vibrational level  $v$  is thus given by

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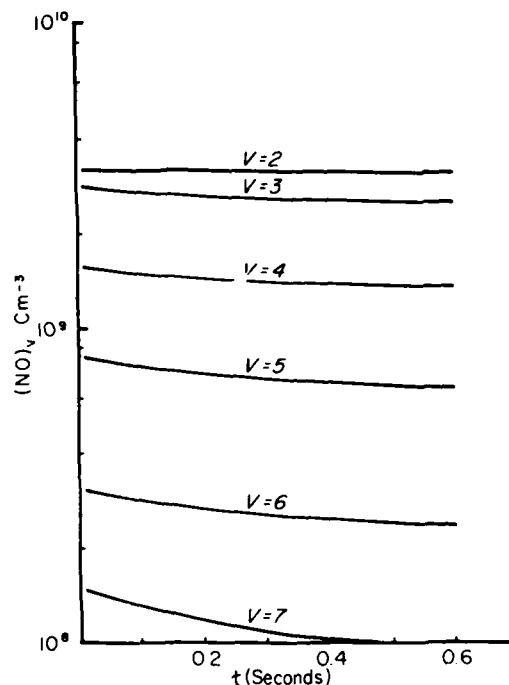


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of vibrational level  $v$ . The derived values of the vibrational rate constants remain the same to within a few percent when the initial number density of nitrogen atoms  $N_0$  is allowed to vary in the computational program by as much as  $\pm 50\%$ . This is gratifying and shows that errors in determining  $N_0$  by titration have no effects on the final results. We have also shown that neglecting the experimental values of the NO concentrations at higher pressures (500 mTorr and up) from the calculations had negligible effect on  $k_1^v$  for all levels and, of course, this would tend to confirm our conclusion above regarding diffusion. If the quenching terms in Eq. (12) are dropped from the calculation, the resulting values of  $k_1^v$  vary by as much as 20% for most levels and thus, in experiments involving the reaction of  $N(^4S)$  with  $O_2$ , the quenching of the product NO by  $O_2$  cannot be neglected. The quenching of  $NO(v)$  by oxygen atoms can have similar effect on the results. Since this quenching rate is not available for all vibrational levels, the effect can be estimated by assuming the rate to be invariant with  $v$  and equal to that of  $NO(v=1) + O \rightarrow NO(v=0) + O$ , which has recently been measured to be  $6.5 \times 10^{-11} \text{ cm}^3/\text{s}$ .<sup>23</sup> Assuming single quantum transitions, calculation yielded the following values (in  $10^{-19} \text{ cm}^3/\text{s}$ ) for  $k_1^v$ : 61, 80, 47, 38, 10, and 8 for  $v=2$  through  $v=7$ , respectively. Comparison with values in Table II shows that with oxygen atom quenching included, NO formation rate constants are increased and increases are slightly larger for higher vibrational levels.

Regarding the mechanism responsible for formation of  $N_2O$ , this molecule can possibly be formed in the standard kinetic mechanism of Reaction (5) forming  $NO_2$  which in turn reacts with N to form  $N_2O$  via Reaction (11). The resulting concentrations of  $N_2O$  calculated based upon this mechanism appear to be a factor of 5 lower than the observed concentration quoted above which may be in error anyway (see above).

Finally, to summarize, we have measured the vibrational rate constants for formation of NO in levels  $v=2$  through  $v=7$  in  $N(^4S) + O \rightarrow NO + O$  reaction. Unfortunately, there are no other absolute measurements of these rates for comparison with our results. We have made reasonably sure that our observations indeed measured emission from NO formed in this reaction and that spectral contamination was eliminated. Nevertheless, further research is needed. It appears that measurement of these rates through observation of the NO fundamental at  $5.4 \mu\text{m}$  would be very illuminating in addition to providing rate constants for ground and first vibrational levels.

## ACKNOWLEDGMENTS

The authors express their appreciation to Dr. R. E. Murphy for generous help in the use of the interferometer. They are also grateful to G. E. Caledonia of Physical Sciences, Inc., Woburn, Mass. for very helpful discussions. Assistance in the design and construction of the experimental apparatus by C. P. Dolan is also gratefully acknowledged. This work derived parallel support from AFOSR Task 2303G2.

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of vibrational level  $v$ . The derived values of the vibrational rate constants remain the same to within a few percent when the initial number density of nitrogen atoms  $N_0$  is allowed to vary in the computational program by as much as  $\pm 50\%$ . This is gratifying and shows that errors in determining  $N_0$  by titration have no effects on the final results. We have also shown that neglecting the experimental values of the NO concentrations at higher pressures (500 mTorr and up) from the calculations had negligible effect on  $k_1^v$  for all levels and, of course, this would tend to confirm our conclusion above regarding diffusion. If the quenching terms in Eq. (12) are dropped from the calculation, the resulting values of  $k_1^v$  vary by as much as 20% for most levels and thus, in experiments involving the reaction of  $N(^4S)$  with  $O_2$ , the quenching of the product NO by  $O_2$  cannot be neglected. The quenching of  $NO(v)$  by oxygen atoms can have similar effect on the results. Since this quenching rate is not available for all vibrational levels, the effect can be estimated by assuming the rate to be invariant with  $v$  and equal to that of  $NO(v=1) + O \rightarrow NO(v=0) + O$ , which has recently been measured to be  $6.5 \times 10^{-11} \text{ cm}^3/\text{s}$ .<sup>23</sup> Assuming single quantum transitions, calculation yielded the following values (in  $10^{-19} \text{ cm}^3/\text{s}$ ) for  $k_1^v$ : 61, 80, 47, 38, 10, and 8 for  $v=2$  through  $v=7$ , respectively. Comparison with values in Table II shows that with oxygen atom quenching included, NO formation rate constants are increased and increases are slightly larger for higher vibrational levels.

Regarding the mechanism responsible for formation of  $N_2O$ , this molecule can possibly be formed in the standard kinetic mechanism of Reaction (5) forming  $NO_2$  which in turn reacts with N to form  $N_2O$  via Reaction (11). The resulting concentrations of  $N_2O$  calculated based upon this mechanism appear to be a factor of 5 lower than the observed concentration quoted above which may be in error anyway (see above).

Finally, to summarize, we have measured the vibrational rate constants for formation of NO in levels  $v=2$  through  $v=7$  in  $N(^4S) + O \rightarrow NO + O$  reaction. Unfortunately, there are no other absolute measurements of these rates for comparison with our results. We have made reasonably sure that our observations indeed measured emission from NO formed in this reaction and that spectral contamination was eliminated. Nevertheless, further research is needed. It appears that measurement of these rates through observation of the NO fundamental at  $5.4 \mu\text{m}$  would be very illuminating in addition to providing rate constants for ground and first vibrational levels.

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